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# Ab-initio Estimation of Solvation Effect, Thermodynamic and Spectroscopic analysis of Salicylic Acid

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## Abstract

Salicylic acid ($C_7H_6O_3$) is an important compound (phenolic) used in the manufacture of pharmaceuticals, textiles, and skin care products. It is also used as a preservative. In the present study, the Density functional theory (DFT) method was used with 6-311++G (d,p) basis set and B3LYP to investigate solvation effects of gas phase, benzene, chloroform, dichloro-methane, dimethyl-sulfoxide (DSMO), and water on salicylic acid. We also investigated the bond length, bond angle, frontier molecular orbital energies (FMOE), global quantities, nonlinear optical properties, and thermodynamic properties of Salicylic acid in these solvents. The analysis of the HOMO-LUMO band gap revealed an increasing trend with solvent polarity, with water exhibiting the highest stability at 4.7928 eV. Ionization potentials (IPs), electron affinities (EAs), and global chemical indices all exhibited a direct relationship with solvent polarity. In addition, we investigated the nonlinear optical properties such as dipole moment, anisotropic polarizability, as well as mean hyper-polarizability. Results show an increase with solvent polarity of these mentioned parameters, while mean polarizability decreases with increase in solvent polarity. On the other hand, the thermodynamic properties analysis unveiled that heat capacity and entropy increased with solvent polarity, whereas zero-point vibrational energy decreases with solvent polarity. This comprehensive investigation sheds light on the intricate interplay between solvent polarity and the structural, electronic, and thermodynamic properties of Salicylic acid, providing valuable insights for future studies in Physics, solvation Chemistry and Material science.

**Keywords:** Salicylic acid, Density Functional Theory, Polarizability, DSMO

## 1. Introduction

Salicylic acid (SA), recognized as ortho-hydroxybenzoic acid, is a prominent phenolic compound within the plant kingdom. It stands out as a member of a varied group of such compounds, known for their significance and prevalence in plant (Onouchi et al., 1995). A substance that possess an aromatic ring bearing hydroxyl group or its functional derivative isolated from willow bark in the early 1800s (An and Mou, 2011). Salicylic acid is an important organic compound with unique properties making it applicable in different industries. It is use as a preservative, in the manufacture of pharmaceuticals, textiles and skin care products due to its protective properties and dermatological effect (Özokan et al., 2022). Salicylic acid and its derivatives are applied to ease pain, reducing fever, treating inflammation, helping prevent heart issues, and are being studied for their possible role in fighting tumors (Onouchi et al., 1995). In addition, salicylic acid also plays crucial roles in plant growth and development, influencing processes such as flower formation, ion uptake, and hormone synthesis, as demonstrated by Grimes (2006).

For decades, extensive experimental and theoretical studies were conducted on salicylic acid to explore its structure and properties under different conditions. For example, the authors of (El Ouafy et al., 2022) applied ab initio methods to examined the electronic structure, electronic properties and nonlinear optical properties of salicylic acid. In another study conducted by (Farajtabar and Gharib, 2010), spectrophotometry and potentiometric methods were used to investigated how the acidity of salicylic acid changes in different mixtures of water and DMSO (dimethyl sulfoxide). (Lim et al., 2013) employed experimental measurements and computational modeling to determine the solubility of salicylic acid in various alcohols, revealing the preferential solvation of salicylic acid by water in water-rich mixtures and by ethanol in ethanol-rich mixtures. In addition, mathematical models such as the Jouyban-Acree model can estimate the behavior of salicylic acid in different mixtures with good precision (Akay et al., 2023). In the 20th century, computational and ab-initio methods have proven worthy (e.g. Density Functional Theory (DFT) and Hartree Fork (HF)) in estimating the behavior of compounds and molecules, especially properties relative to structure, vibrations, and electronic properties. For example, the authors of (Suresh et al., 2014) were able to get correlating outcomes between experimental and ab-inition results while studying the molecular vibrations, stability, and electronic properties, of SA.

The solubility of salicyclic acid in different solvents have also received attention in recent decade. The authors of (Khezri et al., 2023) studied the interaction of salicylic acid with different polyethylene glycols (PEGs) of varying molar masses (200 to 600 g/mole) at temperatures ranging from 293.15 to 313.15 K. Their results show that; the solubility of salicylic acid decreased with lower PEG molar mass and temperature. (Maheshwari et al., 1999) applied quantum computational methods to examine how protons move within salicylic acid molecules in both their normal and excited states. (Sobolewski and Domcke, 2006) applied quantum computational methods to study the significance of hydrogen transfer and changes in the carboxyl group's structure in reaction paths involving SA($C7H6O3$). Their results reveal the ability of salicylic acid to transition to a planar state and reach a conical intersection with the ground state, leading back to its original form when it is in the excited state. Moreover, in an extensive review conducted by (Arif, 2015) on salicylic acid as a peeling agent, shows that it is particularly effective for acne due to its ability to unclog pores by disrupting cellular junctions rather than breaking down keratin filaments making it safe and effective for various skin types and conditions, including acne, melasma, and photo-damage. Using green chemistry methods, salicylic acid was synthesized in which it was made from natural wintergreen oil, with optimization of synthesis parameters obtaining high-purity salicylic acid for cosmetics within a short frame of time (Özokan et al., 2022). Furthermore, in a computational analysis carried out by (Sarasia et al., 2012), the stability and acidic properties of salicylic acid derivatives were analyzed along with their excitation parameters at different temperatures. The results offer insights into their biochemical functionality and structural features, aiding further research on molecules with enhanced drug properties.

Until the time of developing this study, the thermodynamic effects of solvents on salicylic received very little attention. Especially the solvent effects which may also affect the nonlinear optical properties of SA($C7H6O3$). Therefore, in this study, we aim to investigate the solvation behavior of salicylic acid in various solvents. We in addition aim to characterize the thermodynamic parameters associated with these solvation processes, as well as evaluating the nonlinear optical properties of solvated salicylic acid compound. All this would be done theoretically by applying quantum mechanical estimations (DFT method with basis set 6-311++G (d,p)). Through theoretical calculations, we seek to deepen our understanding of the behavior and interaction as well as the stability and reactivity of the compound, contributing to its rational design and application in diverse fields.

## 2. Methods

We employed Gaussian 09W software to do all theoretical calculations and analysis (cite gaussian). The effects of solvents as well as the thermodynamics and nonlinear optical properties of salicylic Acid (C7H6O3) are the main interest of this study. These properties and effects are explored theoretically using Density Functional Theory (DFT). DFT is a significant method in computational chemistry. it is often preferred for its speed compared to other methods, providing efficient results (HAMAD et al., 2023). In the tradition of ab-initio methods, the molecule under investigation needs to be optimized. This is done to achieve a ground state level of the molecule. The basis set 6-311++G(d,p) with B3LYP was able to achieve the minimum ground state energy of SA. The optimized molecule is used for the analysis of the effect of five different solvents, which include water, benzene, chloroform, DSMO, dichloro-methane as well as in the gas phase. To investigate solvation effects, we utilized a Self-Consistent Reaction Field (SCRF) method grounded in the Polarizable Continuum Model (PCM). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were obtained and the Bandgap energy in electron volt (eV) was calculated for all the solvents, which is the difference between the HOMO and LUMO (Eq 1).

$$E_{gap} = E_{LUMO} - E_{HOMO} \approx IP - EA \qquad (1)$$

### 2.1 Global Quantities

Apart from the energy band gap, there are other global reactivity descriptors such as chemical potential, global hardness, global softness, electronegativity and electrophilicity index. These parameters are used in quantum computational methods to predict the behaviour of a chemical species. According to (Plakhutin and Davidson, 2009), the highest occupied molecular orbital (Eq 2) energy is also equal to the (negative of) first ionization energy (I) of the molecule. While on the other hand, the lowest unoccupied molecular orbital (Eq 3) energy is equal to the (negative of) the electron affinity (A) of the molecule. Hence, the ionizing energy and electron affinity state of a molecule related to its E_HOMO and E_LUMO values.

$$IP = -E_{HOMO} \qquad (2)$$

$$EA = -E_{LUMO} \qquad (3)$$

Global hardness is given by half of the energy band gap (Oyeneyin, 2017);

$$\eta = \frac{IP-EA}{2} \qquad (4)$$

The inverse of the hardness is expressed as the global softness as (Yang and Parr, 1985);

$$S = \frac{1}{\eta} \qquad (5)$$

The chemical potential is given by (Khan et al., 2017);

$$\mu = -\left(\frac{IP+EA}{2}\right) \qquad (6)$$

The electronegativity is given by (Khan et al., 2017);

$$\chi = \frac{IP+EA}{2} \tag{7}$$

The electrophilic index expressed as

$$\omega = \frac{\mu^2}{2\eta} \tag{8}$$

The global electrophilicity index (ω) evaluates the susceptibility of a chemical species (atom, molecule, or ion) to gain electrons, which is used to predict the reactivity of a nucleophile in a chemical reaction (Parr et al., 1999). Moreover, the ω index quantifies the energy loss between receivers and transmitters, relative to the total energy transferred (Kiyooka et al., 2013). A higher ω index indicates a stronger electrophile, while a lower ω index indicates a stronger nucleophile. Thus, a good nucleophile is described by lower values of ω (Marinho et al., 2021).

## 2.2 Nonlinear optical properties

In the determination of nonlinear optical properties of a molecule, it is essential to employ extensive basis sets, as well as adopting a sophisticated theoretical approach. Specifically, these basis sets should encompass ‘d’ and ‘p’ polarization functions in conjunction with ‘s’ and ‘p’ diffuse functions (Gidado et al., 2021). The basis set chosen during the optimization process (6-311++G (d,p)) was able to meet these requirements. In addition to this, the mean polarizability, anisotropy polarizability, dipole moment and mean hyper-polarizability of Salicylic acid were calculated.

The dipole moment is a property utilized to describe the polarity of a system which can be obtain from (Obi-Egbedi et al., 2015);

$$\mu_{tot} = \left[\mu_x^2 + \mu_y^2 + \mu_z^2\right]^{1/2} \tag{9}$$

Where μ_x,μ_u and μ_z are the components of the dipole moment in x, y, and z coordinates.

Polarizability is a measure of how easily the electron cloud around an atom or molecule can be distorted by an electric field. Determining the polarizability of a molecule or compound relies on the crucial property of electric dipole polarizability. It's a way of measuring how much a molecule responds to a small electric field, showing the second-order change in energy (Abdulaziz et al., 2019).

$$\alpha = -\frac{\partial^2 E}{\partial F_a \partial F_b} \tag{10}$$

Where a, and b are coordinates of x, y, and z. The mean polarizability is calculated using the following equation.

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \tag{11}$$

The quantities α_xx≤α_yy≤α_zz known as principal values of polarizability tensor. This property is used to measures the strength of molecular interactions (Obi-Egbedi et al., 2015); The anisotropy of polarizability is given by (Khan et al., 2017);

$$\Delta\alpha = \left[\frac{\left(\alpha_{xx}-\alpha_{yy}\right)^2+\left(\alpha_{yy}-\alpha_{zz}\right)^2+\left(\alpha_{zz}-\alpha_{xx}\right)^2+6\left(\alpha_{xz}^2+\alpha_{xy}^2+\alpha_{yz}^2\right)}{2}\right]^{1/2} \qquad 12)$$

The mean first hyper polarizability is given as (Khan et al., 2017);

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{13}$$

*Where β_x, β_y and β_z are defined as:*

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \tag{14}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \tag{15}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \tag{16}$$

β_x, β_y and β_z refer to the components of hyper-polarizability along x, y and z components of molecular dipole moment obtained from the Gaussian output file.

# 3. Results

## 3.1. Geometry Optimization

The geometry optimization technique calculates the energy at an initial geometry of a molecule and then proceed to search a new geometry with a lower energy in which various methods such as semi-empirical, Density Functional Theory, Molecular Mechanics and Hartree–Fock are used (Bálint and Jäntschi, 2021). Density Functional theory with B3LYP/6-311++G (d,p) was used to achieve more complex geometry enhancements of the compound in the gas phase and in different solvents (water, benzene, chloroform, DSMO, dichloro-methane). Optimized values of bond lengths and bond angles of the studied compound were calculated, and the result are presented in Table 1 and 2. The term bond length refers to the distance between the nuclei of two atoms that are bonded together. On the other hand, bond angle denotes the angle formed between two adjacent bonds of an atom within a molecule (Abdulaziz et al., 2019). Stability of a compound increases with increase in bond angle. The largest bond angle was found to be 124.4808° in the gas phase making it the most stable while, the smallest was also found in gas phase which is 106.9028°. The strongest bonds are characterized by the shortest bond distances, while the weakest bonds exhibit the longest bond distances (Gidado et al., 2021). The result in Tables 1&2 show that, the shortest bond distance is 0.9687Å in gas phase, which is the strongest bond while the longest bond distance is 1.4667Å, which is the weakest bond in water. Very little changes are seen in the bond length and bond angle when optimized with different solvents.

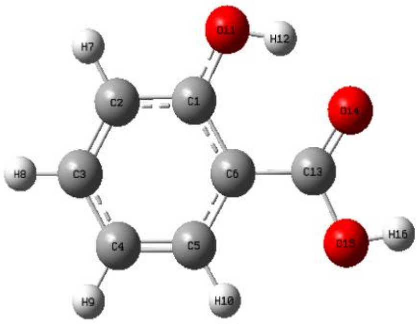

**Figure 1:** Optimized geometry of salicylic acid

**Table 1**: Bond lengths (Å) of the optimized structure of salicylic acid in the gas phase and in different solvents

| Bondlength(Å) | Gasphase | Benzene | Chloroform | Dichloromethane | DSMO | Water |
|---|---|---|---|---|---|---|
| R(1,2) | 1.4017 | 1.4010 | 1.4006 | 1.4005 | 1.4003 | 1.4002 |
| R(1,6) | 1.4174 | 1.4169 | 1.4168 | 1.4167 | 1.4166 | 1.4166 |
| R(1,11) | 1.3429 | 1.3457 | 1.3472 | 1.3481 | 1.3490 | 1.3491 |
| R(2,3) | 1.3845 | 1.3853 | 1.3857 | 1.3860 | 1.3863 | 1.3863 |
| R(2,7) | 1.0830 | 1.0831 | 1.0831 | 1.0832 | 1.0832 | 1.0832 |
| R(3,4) | 1.4023 | 1.4021 | 1.4021 | 1.4020 | 1.4020 | 1.4020 |
| R(3,8) | 1.0845 | 1.0843 | 1.0842 | 1.0842 | 1.0841 | 1.0841 |
| R(4,5) | 1.3826 | 1.3831 | 1.3834 | 1.3836 | 1.3838 | 1.3838 |
| R(4,9) | 1.0829 | 1.0828 | 1.0828 | 1.0828 | 1.0828 | 1.0828 |
| R(5,6) | 1.4078 | 1.4078 | 1.4079 | 1.4079 | 1.4080 | 1.4080 |
| R(5,10) | 1.0822 | 1.0822 | 1.0821 | 1.0821 | 1.0821 | 1.0821 |
| R(6,13) | 1.4642 | 1.4654 | 1.4659 | 1.4663 | 1.4666 | 1.4667 |
| R(11,12) | 0.9813 | 0.9816 | 0.9822 | 0.9825 | 0.9828 | 0.9828 |
| R(13,14) | 1.2260 | 1.2275 | 1.2285 | 1.2290 | 1.2295 | 1.2296 |
| R(13,15) | 1.3488 | 1.3454 | 1.3433 | 1.3422 | 1.3410 | 1.3409 |
| R(15,16) | 0.9687 | 0.9694 | 0.9698 | 0.9700 | 0.9702 | 0.9703 |

**Table 2:** Bond angles (˚) of the optimized structure of salicylic acid in the gas phase and in different solvents

| Bondlength (Å) | Gasphase | Benzene | Chloroform | Dichloromethane | DSMO | Water |
|---|---|---|---|---|---|---|
| A(2,1,6) | 119.2440 | 119.3645 | 119.4257 | 119.4610 | 119.4951 | 119.4993 |
| A(2,1,11) | 117.7235 | 117.7545 | 117.7738 | 117.7868 | 117.8030 | 117.8042 |
| A(6,1,11) | 123.0325 | 122.8810 | 122.8005 | 122.7522 | 122.7018 | 122.6965 |
| A(1,2,3) | 120.2183 | 120.1857 | 120.1695 | 120.1612 | 120.1520 | 120.1507 |
| A(1,2,7) | 118.1882 | 118.3505 | 118.4528 | 118.5077 | 118.5666 | 118.5731 |
| A(3,2,7) | 121.5935 | 121.4638 | 121.3777 | 121.3311 | 121.2814 | 121.2761 |
| A(2,3,4) | 121.0129 | 120.9647 | 120.9410 | 120.9253 | 120.9113 | 120.9097 |
| A(2,3,8) | 119.2371 | 119.2437 | 119.2512 | 119.2568 | 119.2611 | 119.2613 |
| A(4,3,8) | 119.7500 | 119.7916 | 119.8078 | 119.8179 | 119.8276 | 119.8290 |
| A(3,4,5) | 119.2993 | 119.3249 | 119.3391 | 119.3467 | 119.3539 | 119.3548 |
| A(3,4,9) | 120.3780 | 120.3748 | 120.3674 | 120.3637 | 120.3588 | 120.3587 |
| A(5,4,9) | 120.3228 | 120.3003 | 120.2935 | 120.2896 | 120.2873 | 120.2864 |
| A(4,5,6) | 120.8716 | 120.8860 | 120.8953 | 120.9017 | 120.9063 | 120.9066 |
| A(4,5,10) | 120.5486 | 120.4549 | 120.3950 | 120.3623 | 120.3305 | 120.3267 |
| A(6,5,10) | 118.5798 | 118.6591 | 118.7097 | 118.7360 | 118.7632 | 118.7667 |
| A(1,6,5) | 119.3539 | 119.2741 | 119.2294 | 119.2041 | 119.1814 | 119.1788 |
| A(1,6,13) | 118.8999 | 119.0040 | 119.0756 | 119.1088 | 119.1377 | 119.1405 |
| A(5,6,13) | 121.7462 | 121.7219 | 121.6950 | 121.6871 | 121.6810 | 121.6807 |
| A(1,11,12) | 108.0551 | 107.8955 | 107.7553 | 107.6913 | 107.6279 | 107.6211 |
| A(6,13,14) | 124.4808 | 124.2619 | 124.1200 | 124.0485 | 123.9683 | 123.9602 |
| A(6,13,15) | 114.8126 | 114.7958 | 114.8030 | 114.7991 | 114.8034 | 114.8027 |
| A(14,13,15) | 120.7066 | 120.9422 | 121.0771 | 121.1524 | 121.2284 | 121.2371 |
| A(13,15,16) | 106.9028 | 107.5063 | 107.8599 | 108.0342 | 108.2093 | 108.2269 |

### 3.2. Frontier Molecular Orbital Energies (FMOEs)

The concepts of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are important in chemistry. HOMO can donate an electron while LUMO can accept an electron. The description of chemical behaviour and molecular stability is commonly achieved through the extensive application of molecular orbital theory (Borah and Devi, 2018). The obtained energy band gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness-softness of a molecule (Pegu, 2014). Compounds with larger HOMO LUMO band gap tends to be unreactive and high in stability (HSSAIN, 2022). Figure 2 shows the order of increasing solvent polarity from up to down with gas phase being the less polar and water being higher in polarity among the solvents. As seen, the order of stability of salicylic acid is less in the gas phase and higher in water, which shows an increase with increase in polarity of the solvents. The order of stability of a compound increases with increase in polarity of the solvents (Ismail et al., 2019). The HOMO-LUMO gap (4.744eV) calculated in gas phase using Eq 1 is found to be very close to 4.742 eV of salicylic acid reported by (El Ouafy et al., 2022). Figure 3 shows the effect of all the solvents used on the band gap of salicylic acid compound. It is also observed that as the polarity of the solvent increases the band gap also increases with water having the highest value of 4.7928 eV and gas phase having the lowest value of 4.7437 eV.

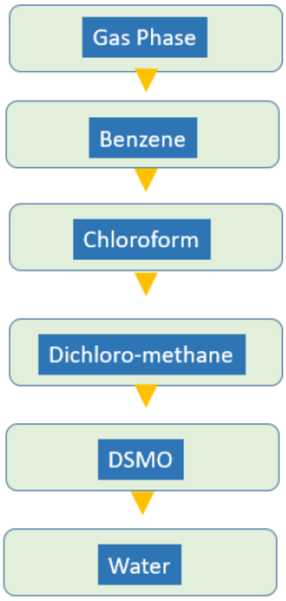

**Figure 2:** The order of increasing solvent polarity.

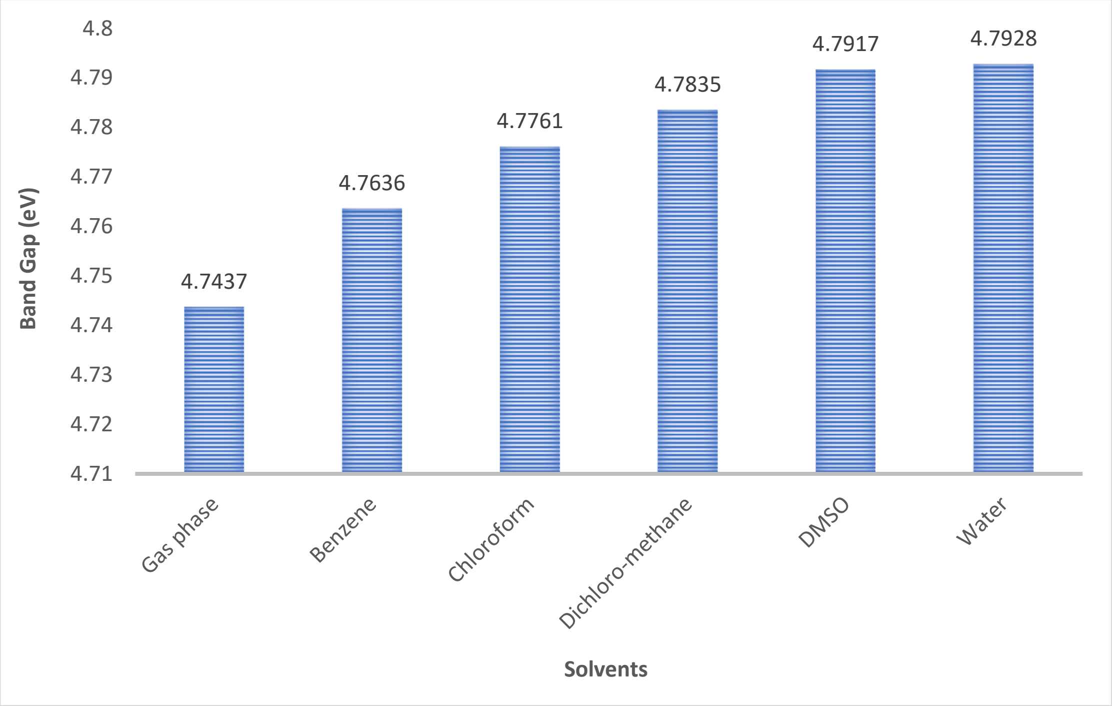

**Figure 3:** Plot of band gap in eV against solvents

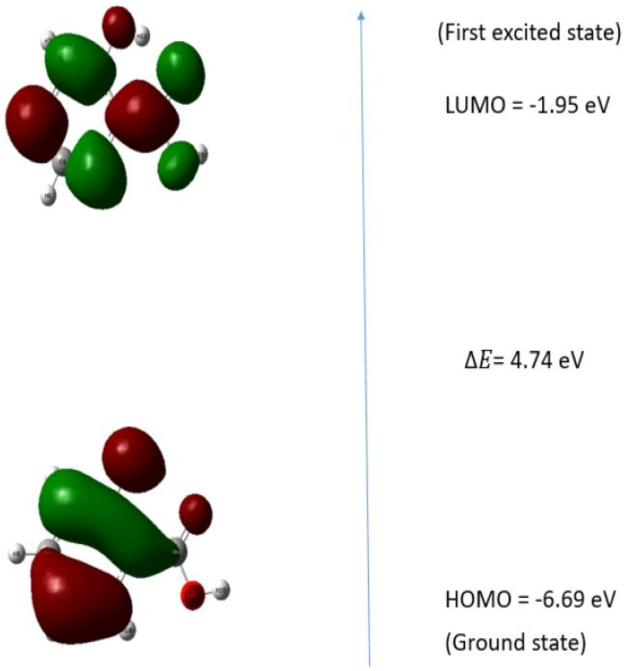

**Figure 4**: Contour diagram of frontier orbitals, computed in the gas phase with 6-311++G (d,p) basis set and B3LYP of DFT of Salicylic acid compound.

**Table 3:** Calculated HOMO, LUMO and energy gap in eV of the optimized structure of salicylic acid

| Solvents | EHOMO | ELUMO | Band gap |
|---|---|---|---|
| Gas phase | -6.6920 | -1.9483 | 4.7437 |
| Benzene | -6.7095 | -1.9459 | 4.7636 |
| Chloroform | -6.7302 | -1.9540 | 4.7761 |
| Dichloro-methane | -6.7435 | -1.9600 | 4.7835 |
| DSMO | -6.7590 | -1.9674 | 4.7917 |
| Water | -6.7610 | -1.9679 | 4.7928 |

### 3.3 Ionization potentials (IPs), electron affinities (EAs) Global chemical indices

Ionization potential (IP) and electron affinity (EA) are well-defined properties that describe the electronic structure of materials. These properties measure the tendency of compounds to lose or gain an electron (Kumer et al., 2017). The determination of various chemical reactivity parameters, serving as indicators of relative stability and reactivity, relies on the energies of frontier orbitals HOMO and LUMO. Table 4 presents such parameters which include Ionization potentials (IP), electron affinity (EA), the chemical potential ($\mu$), global hardness ( $\eta$), global softness (S), electronegativity (χ) and electrophilicity (ω).

The higher the value of ionization potential (IP), the more difficult it is to remove an electron to form an ion. The lower the value of electron affinity (EA), the less easy it is to add an electron (Ismail et al., 2019). Table 4 shows that the value of ionization potential obtained using Eq(2) increases with increase in polarity of the solvents, and it is most difficult to remove an electron in water and less difficult do so in the gas phase. It is also observed that the value of electron affinity obtained using Eq(3) increases with increase in polarity of the solvents, and it is most difficult to add an electron in water and less difficult to do so in the gas phase.

Chemical hardness and softness provide information about the reactivity and stability of a molecule. Increase in chemical hardness makes a molecule more stable and less reactive. As observed from the table 4, the value of chemical hardness calculated using Eq(4) increases with increase in solvent polarity with water having the highest value of hardness ($\eta$ =2.3964 eV), which is more stable and less reactive. The gas phase having the highest value of softness (S =0.4216 eV) calculated using Eq (5) decreases with increase in polarity of the solvents. Electronegativity is the ability of a molecule to attract an electron. As value of electronegativity is increased, atoms and molecules have a larger capacity to attract electrons to themselves with water having the highest value of electronegativity (χ = 4.3643 eV) obtained using Eq 7. The chemical potential (μ) in electron volts quantifies the propensity of an electron to escape and is correlated with molecular electronegativity. A more negative μ indicates increased difficulty in electron loss but enhanced ease in electron gains with water having highest negative value of -4.3643 eV calculated using Eq(6). The ω index quantifies the energy loss between receivers and transmitters, relative to the total energy transferred (Kiyooka et al., 2013). A higher ω index indicates a stronger electrophile, while a lower ω index indicates a stronger nucleophile. Thus, a good nucleophile is described by lower values of ω (Marinho et al., 2021). The result shows that salicylic acid in water solvent has highest value of ω = 3.9741 eV calculated using Eq (8) making it good electrophile while salicylic acid in benzene solvent having the lowest value of ω = 3.9316 eV making it a good nucleophile.

**Table 4:** Ionization potentials (IPs), electron affinities (EAs) and Global chemical indices of the optimized salicylic acid in the gas phase and in different solvents

| Solvents | IP(eV) | EA(eV) | $\eta$(eV) | S(eV) | χ(eV) | $\mu$(eV) | ω(eV) |
|---|---|---|---|---|---|---|---|
| Gas phase | 6.6920 | 1.9483 | 2.3719 | 0.4216 | 4.3202 | -4.3202 | 3.9344 |
| Benzene | 6.7095 | 1.9459 | 2.3818 | 0.4198 | 4.3277 | -4.3277 | 3.9316 |
| Chloroform | 6.7302 | 1.9540 | 2.3880 | 0.4187 | 4.3421 | -4.3421 | 3.9475 |
| Dichloro-methane | 6.7435 | 1.9600 | 2.3917 | 0.4181 | 4.3518 | -4.3518 | 3.9590 |
| DSMO | 6.7590 | 1.9674 | 2.3958 | 0.4174 | 4.3632 | -4.3632 | 3.9730 |
| Water | 6.7610 | 1.9679 | 2.3964 | 0.4173 | 4.3643 | -4.3643 | 3.9741 |

## 3.4 Nonlinear optical properties

To expand the study of the applications of salicylic acid, the effects of solvent on nonlinear optical (NLO) properties were investigated. Table 5 shows the nonlinear optical properties of salicylic acid in gas phase and in different solvents. The properties investigated include dipole moment, mean polarizability, anisotropic polarizability and mean hyper polarizability. A dipole moment is a measure of the separation of positive and negative electrical charges within a molecule. Table 5 shows the dipole moment obtained using Eq (9) which increases with increase in solvent polarity with gas phase having the smallest dipole moment. Increase and decrease of solvent polarity plays an effective role on the nonlinear optical properties of a molecule. Mean polarizability is the average ability of molecules to respond to an external electric field by redistributing their electron density. It is a crucial parameter in understanding the behavior of molecules in different solvents. From table 5, our result obtained by applying Eq (11) indicates that mean polarizability decreases as solvent polarity increases. This suggests that the ability of molecules to respond to an external electric field diminishes in more polar solvents with water having the lowest value. The anisotropy of polarizability of the compound calculated using Eq (12) was found to increase with increase in solvent polarity with water having the highest value. In addition, we observed that solvent polarity exerts a significant influence on the first hyper-polarizability, which increased with increase in solvent polarity water having the highest value and the gas phase having the smallest value.

**Table 5:** Non-linear optical properties (in Debye) of the optimized salicylic acid compound in the gas phase and different solvents

| Solvents | $\boldsymbol{\mu_{tot}}$ | $\boldsymbol{\alpha}$ | $\boldsymbol{\Delta\alpha}$ | $\boldsymbol{\beta_{tot}}$ |
|---|---|---|---|---|
| Gas phase | 2.2449 | -55.9503 | 12.9488 | 40.5519 |
| Benzene | 2.6186 | -55.7093 | 14.0436 | 41.8281 |
| Chloroform | 2.8519 | -55.5639 | 14.6938 | 42.8390 |
| Dichloro-methane | 2.9790 | -55.4852 | 15.0395 | 43.4506 |
| DSMO | 3.1115 | -55.4032 | 15.3949 | 44.1339 |
| Water | 3.1251 | -55.3947 | 15.4310 | 44.2075 |

## 3.4 Thermodynamic properties

Table 6 highlights the electronic, translational, rotational, and vibrational energies, along with their respective contributions, are presented for the entropy (S) and heat capacity ($C_v$). Additionally, the table includes information on the rotational constants and zero-point vibrational energies (ZPVE) of salicylic acid in both the gas phase and various solvents. It can be observed from the table that the specific heat capacity and entropy increases with increase in solvent polarity while the zero-point vibrational energy decreases with increase in polarity of the solvents.

**Table 6:** Thermodynamic properties of the optimized structure of salicylic acid in the gas phase and different solvents

| | **Gas phase** | | **Benzene** | | **Chloroform** | | **Dichloro-methane** | | **DSMO** | | **Water** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Positions** | $C_v$ | **S** | $C_v$ | **S** | $C_v$ | **S** | $C_v$ | **S** | $C_v$ | **S** | $C_v$ | **S** |
| Electronic | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Translational | 2.981 | 40.679 | 2.981 | 40.679 | 2.981 | 40.679 | 2.981 | 40.679 | 2.981 | 40.679 | 2.981 | 40.679 |
| Rotational | 2.981 | 29.328 | 2.981 | 29.328 | 2.981 | 29.328 | 2.981 | 29.328 | 2.981 | 29.328 | 2.981 | 29.328 |
| Vibrational | 24.956 | 17.489 | 25.009 | 17.551 | 25.038 | 17.577 | 25.057 | 17.594 | 25.075 | 17.608 | 25.077 | 17.610 |
| Total | 30.918 | 87.495 | 30.971 | 87.558 | 31.000 | 87.584 | 31.018 | 87.601 | 31.037 | 87.615 | 31.039 | 87.617 |
| Rotational Constants (GHz) | 2.34068 | | 2.34070 | | 2.34046 | | 2.34048 | | 2.34054 | | 2.34055 | |
| | 1.22190 | | 1.22178 | | 1.22172 | | 1.22165 | | 1.22160 | | 1.22160 | |
| | 0.80281 | | 0.80276 | | 0.80270 | | 0.80268 | | 0.80267 | | 0.80266 | |
| ZPVE (Kcal/ Mol) | 75.33343 | | 75.21155 | | 75.12786 | | 75.08131 | | 75.03220 | | 75.02722 | |

## Remarks

A theoretical investigation was carried out on salicylic acid to understand the effects of solvation on the compound using the B3LYP methods under 6-311++G (d,p) basis set. Our study has provided valuable insights into the solvation behaviour, thermodynamics, and nonlinear optical properties of salicylic acid (SA) in solution-phase environments. The solvation process induces structural changes in salicylic acid and affects its solubility, stability, and reactivity in different solvent systems. The results reveal that the structural properties such as the bond lengths and bond angles increase with increase in solvent polarity in most cases. The strongest bond is found to be in the gas phase and the weakest bond in water. It was observed that the HOMO-LUMO band gap of the compound increases with increase in solvent polarity with water having the highest value of 4.7928 eV, which is most stable. The ionization potentials (IPs), electron affinities (EAs) and global chemical indices all indicated an increase with increase in the polarity of the solvents. The analysis conducted on the nonlinear optical properties of the titled compound such as the dipole moment, mean polarizability, anisotropic polarizability and mean hyper-polarizability were also calculated and reported. . It was observed that dipole moment, anisotropic polarizability and mean hyper-polarizability increases with increase in solvent polarity while mean polarizability decreases with increase in solvent polarity. The analysis conducted on the thermodynamic properties reveals that heat capacity and entropy increases as the polarity of the solvent increases while zero-point vibrational energy decreases with increase in solvent polarity. While this study focused on explaining the solvation-induced changes in Salicylic acid. It wider implications extend to different fields. Understanding the compound's behaviour in different solvent systems enhances our ability to understand its properties for applications ranging from pharmaceutical formulations to environmental cleaning. Future research could explore experimental validations of our theoretical predictions, focusing into the compound's behaviour under conditions in biological environments or industrial processes.

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